Experience of Measurements with a Vibrating-Wire Viscometer on Natural Gases[1]

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A vibrating-wire viscometer designed for high-precision measurements on gases was applied to determine the viscosity coefficient of natural gases. The experiments were carried out at nominal temperatures of 260, 280, 300, and 320 K up to pressures of 20 MPa. A suitable experimental procedure had to be developed in order to minimize the influence of the retrograde behavior and the effects of adsorption and desorption that have to be expected in the thermodynamic range under study. As a consequence, the series of measurements could successfully be performed starting from vacuum followed by successive points up to the maximum pressure. The densities were calculated according to the ISO 12213 standard using the AGA-8 detailed characterization equation. The isotherms could adequately be represented with power series in density restricted to the fourth power. The reproducibility of the measurements was ±0.2%, whereas the uncertainty is estimated to be ±0.5%.

KEY WORDS: gas; measurement; natural gases; vibrating-wire viscometer; viscosity.

1. INTRODUCTION

The viscosity plays an important role in the transfer of natural gas by pipelines and in its flow into or out of underground reservoirs. In these cases the viscosity must be evaluated at operating conditions. This involves a knowledge of the effects of temperature, pressure or density, and composition on the viscosity of the natural gas. Furthermore, the demands

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for reliable viscosity values of natural gases are increasing for engineering design purposes. At first sight the determination of the viscosity of natural gases does not appear to be problematic, because methane as its main constituent occurs supercritically under pipeline conditions. But natural gas contains also high-boiling constituents so that retrograde behavior may be expected. This behavior could give rise to complications in the transportation of natural gas through pipelines as well as during the gas withdrawal from underground storage. But the condensation behavior could possibly also influence the measurement of thermophysical properties, such as the transport coefficients, in corresponding thermodynamic ranges. Within a program aimed to the accurate measurement and correlation of the viscosity of natural gas, this paper presents the experience of developing a suitable experimental method for the determination of the viscosity reducing the influence of the retrograde behavior and the effects of adsorption and desorption as much as possible.

A vibrating-wire viscometer designed to perform measurements of very high precision on gases [1] was recently applied to determine the viscosity of argon, krypton, and propane between 298 and 423 K up to a maximum pressure of 20 MPa [2] as well as the viscosity of methane in the temperature range 260–360 K at pressures up to 29 MPa [3]. This instrument would also be used for measurements on natural gas mixtures according to the experience gained in the investigation of the pure gases mentioned. The thermodynamic range of the experiments – isothermal series of measurements at 260, 280, 300, and 320 K up to pressures of 20 MPa – was chosen with regard to the requirements of the gas industry. It should also be stressed that transport property data for natural gas are not of similar high accuracy as thermodynamic data.

2. EXPERIMENTAL PROCEDURE

The theory of a vibrating-wire viscometer developed by Retsina et al. [4] describes the connection between the parameters of the damped harmonic oscillation of the wire – the logarithmic decrement Δ and the frequency ω – and the properties of the fluid, the density ρ and the viscosity η. The measuring theory is based on the Navier–Stokes equations and on several important conditions which have to be fulfilled. Particularly, the relative initial amplitude ε and the Reynolds number Re should be much smaller than unity.

$$\varepsilon = \frac{y_{\max}}{R} \ll 1, \qquad \Omega = \frac{\rho\,\omega R^2}{\eta}, \qquad Re = \varepsilon\,\Omega \ll 1. \qquad (1)$$

Here y_{max} is the initial amplitude, and R is the radius of the wire. The working equations [1,4] enable the determination of the viscosity η using the measured oscillation parameters Δ and ω provided that the density ρ of the fluid, the density ρ_s and radius R of the wire, and the logarithmic decrement in vacuo Δ_0 are known.

The measurements were carried out with a vibrating-wire viscometer already described and applied by Wilhelm et al. [1], Wilhelm and Vogel [2], and Vogel et al. [3]. The vibrating wire is placed in a magnetic field in such a manner that even harmonics cannot be initiated because of the symmetric arrangement of the wire and field and that the third harmonic mode of the oscillation is suppressed as a result of a ratio of 1.5 between their lengths. The oscillation of the wire is induced by a sinusoidal voltage pulse with a frequency very close to the resonant frequency of the wire. The resulting oscillation is detected by means of the induced voltage which is amplified and measured as a function of time. In general, a hundred oscillation runs are recorded, and the measured oscillation curves are averaged in order to improve the signal-to-noise ratio under the assumption that the noise is asynchronous.

Several improvements compared with the vibrating-wire technique used for liquids [5,6] have been accomplished to have a highly precise instrument for gas viscosity measurements. The application of chromel as the wire material is of importance due to its very smooth surface. It has been shown by Wilhelm et al. [1] that the rough surface of conventionally used tungsten wires leads to systematic errors.

An essential improvement concerns the evaluation of the logarithmic decrement Δ and of the frequency ω deduced from oscillation runs with different relative initial amplitudes ε. Wilhelm et al. [1] have found that Δ and ω depend on the square of the relative initial amplitude. They accounted for this effect in that an important condition for the validity of the measuring theory cannot be kept in real experiments. The signal-to-noise ratio does not become sufficiently large, in practice, if the wire displacement is distinctly smaller than the wire radius according to the requirement of the measuring theory. Therefore, relatively large values of ε are used in different oscillation runs. The correct values of the logarithmic decrement Δ and of the frequency ω are determined by extrapolation of the results for Δ and ω as a function of $\varepsilon^2 \to 0$. Wilhelm et al. have stated that the dependence of Δ and ω on ε^2 is considerably larger at higher densities and almost negligible at low densities due to the density dependence of the Reynolds number. But it is to be stressed that the logarithmic decrement Δ_0 and the frequency ω_0 in vacuo are also slightly dependent on the relative initial amplitude ε.

The experimental equipment is suitable for measurements at pressures up to 40 MPa and at temperatures between 260 and 473 K. The viscometer cell is attached to the top closure of a pressure vessel which is incorporated in a heat-pipe thermostat. The pressure vessel is connected with four transmitters characterized by an uncertainty of 0.01% of reading and 0.01% of full scale. The heat-pipe thermostat is usually filled with water for measurements at the higher temperatures, but for that reported here water was substituted with methanol. The thermostat is heated by means of a heating tape and regulated by a PID controller. For the lower temperatures of 260 and 280 K, a cooling coil was wound around the heat-pipe thermostat and operated by means of a cooling thermostat. The temperature measurements were performed with a premium ITS-90 thermometer and a 6 1/2 digit multimeter. The uncertainty of the temperature is ±0.015 K.

In principle, a vibrating-wire viscometer is an absolute instrument if the wire radius R is known to within an uncertainty of $< 0.1\%$. Unfortunately, this is not the case for wires of such a small radius as applied here. But it is sufficient to determine the radius by measurements using a gas for which the viscosity coefficient is known as accurately as possible for, at least, one thermodynamic state. For this purpose measurements on argon at 298.15 K and for pressures of 0.79 and 1.48 MPa were carried out on the basis of reference values by Kestin and Leidenfrost [7]. The wire radius was determined to be 12.765 μm assuming the value $\rho_s = 8500 \text{ kg} \cdot \text{m}^{-3}$ for the wire density to be true as given by the supplier. The uncertainty of the vibrating-wire viscometer is estimated to be ±0.2% for measurements for which the density is reliably known within ±0.1%. The uncertainty increases dramatically to ±3% close to the critical point, mainly due to the uncertainty of the density resulting from relatively small errors in temperature and pressure. This was shown by Wilhelm and Vogel [2] in the case of propane. The results of the measurements on methane [3] performed nearly in the same temperature and pressure ranges as those on the natural gas reported here have been characterized by a reproducibility of $< \pm 0.1\%$ and by an uncertainty of ±0.3%.

3. MEASUREMENTS AND RESULTS

Four isothermal series of measurements at 260, 280, 300, and 320 K were carried out at pressures up to 20 MPa on two mixture samples of natural gas, H and L, supplied by Ruhrgas AG, Germany.

The densities ρ of the natural gas needed for the evaluation of the viscosity were calculated from the measured temperatures T and pressures

p using the International Standard ISO 12213 *Natural Gas – Calculation of Compression Factor* [8,9]. The evaluation of the densities is based on Part 2 describing a method for use where the detailed molar composition is known. The method is applicable to dry gases of pipeline quality and enables a calculation within an uncertainty of $\pm 0.1\%$ in the temperature range $263\,\mathrm{K} \le T \le 338\,\mathrm{K}$ and at pressures $p < 12\,\mathrm{MPa}$ for given input variables temperature, pressure, and molar composition. The method is also applicable with somewhat increased uncertainty within a wider range of temperatures and to higher pressures. An uncertainty of $\pm 0.2\%$ in the compression factor as well as in the density has been estimated at pressures $p > 11\,\mathrm{MPa}$ for the isotherm at $260\,\mathrm{K}$ and at $p > 18\,\mathrm{MPa}$ for the isotherm at $280\,\mathrm{K}$, whereas the uncertainty limits of $\pm 0.1\%$ should also be valid at pressures up to $20\,\mathrm{MPa}$ for 300 and $320\,\mathrm{K}$, again assuming that the input variables are known with negligible uncertainty. In the molar-composition analysis, constituents to an amount exceeding a mole fraction $x_i > 0.00005$ should at least be taken into consideration. For a typical pipeline quality gas, the sum of the mole fractions of n-octane and higher hydrocarbons may amount to about 0.0005. An additional uncertainty of $\pm 0.1\%$ is to be expected for the case where the uncertainties of the measured temperatures and pressures are approximately $\pm 0.15\,\mathrm{K}$ and $\pm 0.02\,\mathrm{MPa}$, respectively, and that the uncertainties in mole fractions are reasonably small. The method of calculation uses the AGA-8 detailed characterization equation which is an extended virial-type equation. It is described in AGA Report No. 8 [9] and Part 2 of Ref. [8] and applies only to mixtures in the single-phase gaseous state. The molar-composition analysis of samples H and L of natural gas was performed by Ruhrgas AG. The total uncertainty of the calculated densities is estimated to be normally $\pm 0.2\%$ as well as $\pm 0.3\%$ at the higher pressures for low temperatures.

The individual points of a series of measurements cannot be performed exactly at the nominal temperature. Therefore, they are adjusted by means of a Taylor expansion restricted to the first power in temperature and based on the experimental values of the main series of all isotherms (see below). Since the viscosity values at pressures below 0.2 MPa are mostly characterized by a tendency to be too low due to the slip effect, they are not included in the temperature correction function as well as in further evaluation. Thus, a complete series of measurements consisted of 55 points from 0.2 to 20 MPa. They were correlated as a function of the density ρ by means of a power series representation restricted to the fourth power.

$$\eta(T, \rho) = \eta^{(0)}(T) + \eta^{(1)}(T)\,\rho + \eta^{(2)}(T)\,\rho^2 + \eta^{(3)}(T)\,\rho^3 + \eta^{(4)}(T)\,\rho^4. \quad (2)$$

Weighting factors of ρ^{-2} were used in the multiple linear least-squares regression to minimize the relative deviations.

The first series of measurements on sample H of the natural gas were performed according to our experience for measurements on propane [2] and methane [3]. Thus, a series was started with a determination of the parameters of oscillation in vacuo, Δ_0 and ω_0. Then the gas was filled to the maximum pressure. For this purpose the temperature of the bottle with the pressurized gas was increased to about $50\,°C$ by means of heating tapes to avoid condensation of the higher-boiling components of the natural gas during the filling process. After stabilizing the pressure and temperature within $\pm0.005\%$ and $\pm0.01\,K$, a viscosity measurement was carried out. In a further step, the gas was partly released for the next measurement point. Remarkably, the isotherm at $260\,K$ could not be performed down to the lowest pressures, because the vibrating wire did not work in the appropriate manner. A correct measurement and evaluation of the oscillation curves below $3.2\,MPa$ were not possible. It was assumed that condensation of higher-boiling components of the natural gas on the vibrating wire may have occurred (see below). The series of measurements was completed by repeating the vacuum measurement.

In a second series called C additional individual points were measured to check the results of the initial series on sample H. The natural gas pressure was increased starting either from vacuum or from the foregoing control point at lower pressure. Figures 1 and 2 show very large differences up to $+2\%$ and $+1.5\%$ between the measured points of the initial series B and the points of the check series C at 260 and $280\,K$. Consequently, an entire series of measurements was performed again, but from point to point with increasing pressure. These results correspond to the main series A in Figs. 1 and 2.

The results of the initial series of measurements on sample H at $300\,K$ performed for decreasing pressure are compared in Fig. 3 with individual check points of a series C measured again with increasing pressure. The values of the measured points of both series agree within $\pm0.2\%$. Thus, the initial series of measurements was considered to be the main series A at $300\,K$. Similar results were obtained for the isotherm at $320\,K$.

With respect to the experience of the measurements on sample H at 260 and $280\,K$, a complete series of measurements from point to point with increasing pressure was performed on sample L as for main series A for all four isotherms. In addition, individual points were carried out as series C for each isotherm in order to check the results of the main series. The natural gas pressure was increased for these points from vacuum or from the foregoing point.
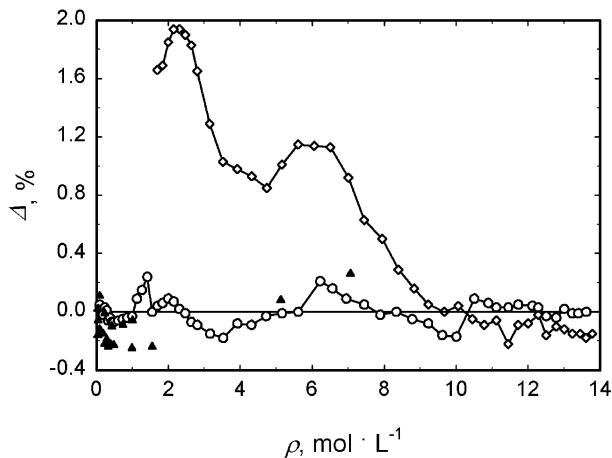
Fig. 1. Deviations [$\Delta = 100(\eta_{exp} - \eta_{cor,seriesA})/\eta_{exp}$] of experimental viscosities of the series of measurements on the natural gas sample H at 260 K from the main series A correlated with Eq. (2). (○) main series A (for increasing pressure), (▲) check series C, (◇) initial series B (for decreasing pressure).
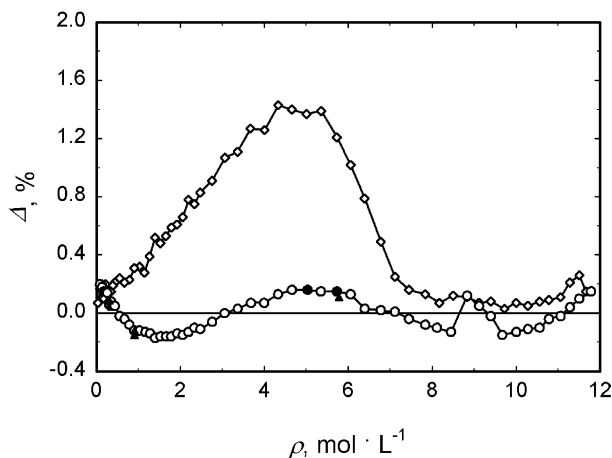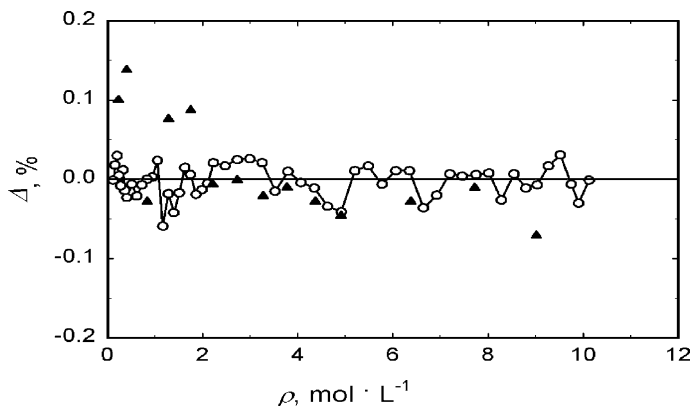

Fig. 2. Deviations [$\Delta = 100(\eta_{exp} - \eta_{cor,seriesA})/\eta_{exp}$] of experimental viscosities of the series of measurements on the natural gas sample H at 280 K from the main series A correlated with Eq. (2). (○) main series A (for increasing pressure), (▲) check series C, (◇) initial series B (for decreasing pressure).

Fig. 3. Deviations $[\Delta = 100(\eta_{exp} - \eta_{cor,seriesA})/\eta_{exp}]$ of experimental viscosities of the series of measurements on the natural gas sample H at 300 K from the main series A correlated with Eq. (2). (○) main series A (for decreasing pressure), (▲) check series C.

Finally, a series of measurements called D was performed for each isotherm to investigate the effects of adsorption and desorption. In this case the natural gas pressure was increased either starting from vacuum or after releasing a certain amount of gas. Subsequent to these points, further measurements were carried out at the same pressure after waiting at least 12 h between the measurement points. The points of series D correspond only approximately to so-called flushing points, but seem to be adequate to investigate the influence of adsorption and desorption.

The results for sample L of the natural gas are shown in Figs. 4–6 for the isotherms at 260, 280, and 320 K as differences related to the results of the main series A.

The weighted percentage standard deviations of the main series A from their representation with Eq. (2) is $< \pm 0.05\%$ for all isotherms of sample L and for the 300 and 320 K isotherms of sample H. The standard deviations are still $< \pm 0.1\%$ for the 260 and 280 K isotherms of sample H. Analogously, the individual percentage deviations are $< \pm 0.1\%$ for the isotherms first mentioned (Figs. 3–6), whereas several measured points of the 280 K isotherm of sample H show deviations up to $\pm 0.2\%$ (Fig. 2) and even a few deviate up to $\pm 0.25\%$ from the fit for the 260 K isotherm of sample H (Fig. 1). The deviations of the check points of series C from the main series A amount to a maximum of $\pm 0.15\%$ for the isotherms of sample L. Apart from some deviations up to $\pm 0.25\%$ for the 260 K isotherm, the measured points of series C for sample H agree within $\pm 0.20\%$ with those of the main series A. Thus, it can be concluded that the
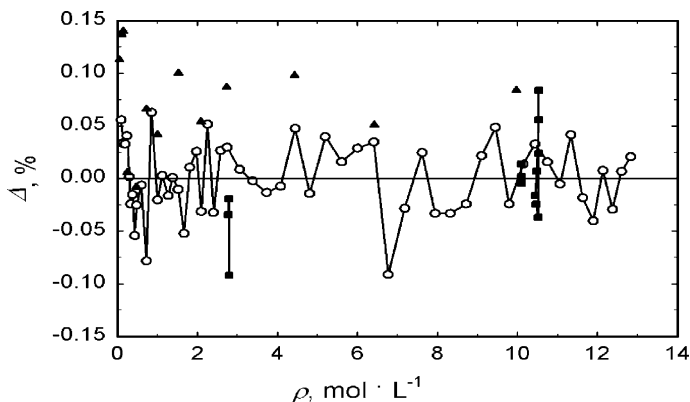
Fig. 4. Deviations $[\Delta = 100(\eta_{exp} - \eta_{cor,seriesA})/\eta_{exp}]$ of experimental viscosities of the series of measurements on the natural gas sample L at 260 K from the main series A correlated with Eq. (2). (○) main series A (for increasing pressure), (▲) check series C, (■) flushing-point series D.
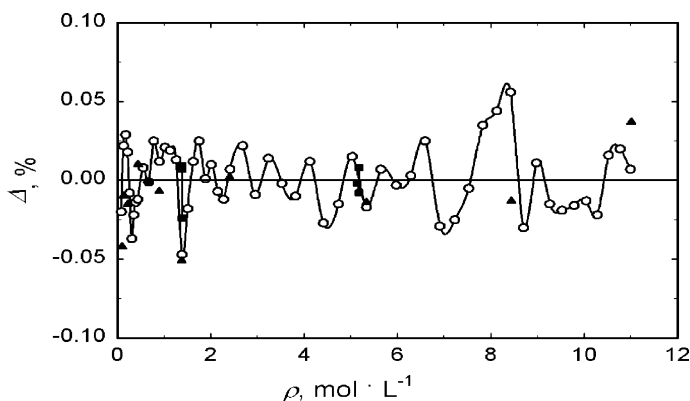

Fig. 5. Deviations $[\Delta = 100(\eta_{exp} - \eta_{cor,seriesA})/\eta_{exp}]$ of experimental viscosities of the series of measurements on the natural gas sample L at 280 K from the main series A correlated with Eq. (2). (○) main series A (for increasing pressure), (▲) check series C, (■) flushing-point series D.

reproducibility of the measurements on both samples of the natural gas is ±0.2%. Considering that the uncertainty of the calculation of the gas density with the AGA8-92DC equation is ±0.2 to ±0.3%, the uncertainty of the measurements is estimated to be ±0.5%.

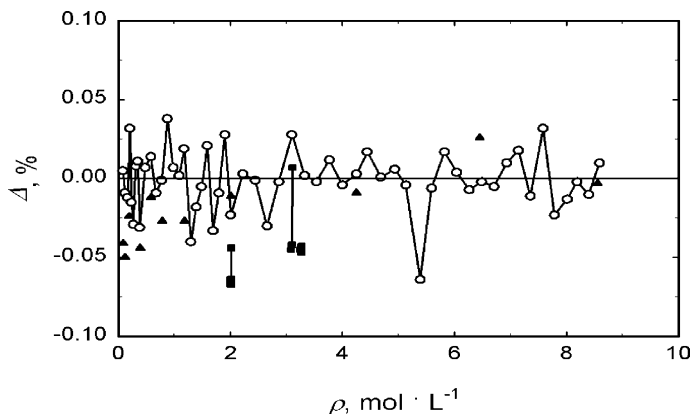**Fig. 6.** Deviations $[\Delta = 100(\eta_{exp} - \eta_{cor,seriesA})/\eta_{exp}]$ of experimental viscosities of the series of measurements on the natural gas sample L at 320 K from the main series A correlated with Eq. (2). (○) main series A (for increasing pressure), (▲) check series C, (■) flushing-point series D.

4. DISCUSSION

The reproducibility and uncertainty of the measurements on the natural gas samples are increased to ± 0.2 and $\pm 0.5\%$ [3], respectively, compared with those of our measurements on methane (± 0.1 and $\pm 0.3\%$). An important reason is that natural gas is a gaseous mixture showing retrograde behavior at low temperatures. Figure 7 demonstrates for sample H that retrograde condensation is to be expected for the lowest isotherms of our measurements at 260 and 280 K. The figure makes clear that the dew-point line is crossed twice if the pressure is decreased along certain isotherms. For example, for 280 K, sample H is a gas at 10 MPa, will partially condense at pressures of about 5.5 MPa, and eventually be a gas again at approximately 0.2 MPa. The higher-boiling components of the natural gas are the main constituents of the condensate. They influence decisively the position of the dew-point line in the corresponding pressure-temperature diagram as shown by Rijkers et al. [10] and by Oellrich et al. [11]. Rijkers et al. investigated experimentally the effect of high-boiling alkanes on the condensation behavior of natural gas. Oellrich et al. calculated dew-point lines for the methane/n-decane binary system dependent on different small admixtures of n-decane as well as dew-point lines for different European samples of natural gas.

The samples H and L under investigation contain up to about 100 ppm of n-octane and higher hydrocarbons. Condensation of such an amount of higher-boiling compounds will not significantly change the
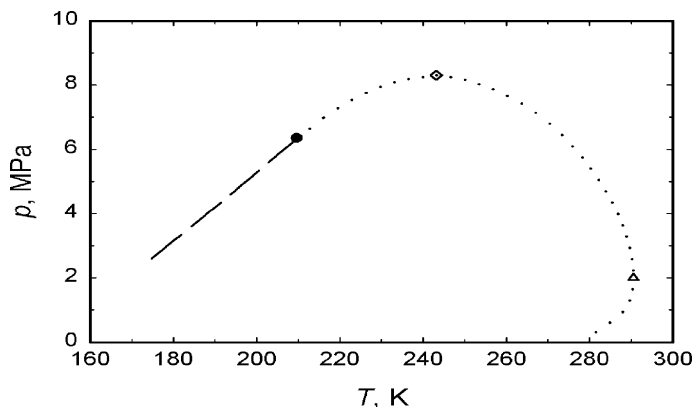
Fig. 7. Pressure–temperature phase envelope of natural gas sample H. (– – –) Bubble-point line, (⋯⋯) dew-point line, (●) critical point, (◇) cricondenbar, (△) cricondentherm.

molar composition of the gas phase. Because the dependence of the viscosity on the molar composition is relatively small, the retrograde condensation will not strongly influence the viscosity value as long as the measurement can be performed in the true gaseous phase assuming that the condensate is deposited or adsorbed at the wall of the measuring vessel. But the viscosity measurement should be affected if the condensate deposit forms on the vibrating wire.

The difference between the results of the main series A of the measurements and those of the series B initially performed for the 260 and 280 K isotherms on sample H should be attributed to the implementation of both series. In series A the natural gas was filled from the bottle at a comparably high temperature (50 °C, see above) supported by the Joule–Thomson effect of the throttle valve. The increase of pressure from the foregoing to the next measurement point ensured that the small condensation is affected by cooling to the temperature of the measuring vessel. Thus, it could be assumed that condensate and gaseous phases are in thermodynamic equilibrium during the viscosity measurement. On the contrary, in series B the release of natural gas from the measuring vessel in order to get one lower pressure should have led to cooling below the temperature of the measuring vessel because of the Joule–Thomson effect and should give rise to relatively severe condensation on the wall of the vessel or on the vibrating wire. The following increase to the temperature of the measuring vessel does not mean that equilibrium between adsorption and desorption is attained during the viscosity measurement. The large
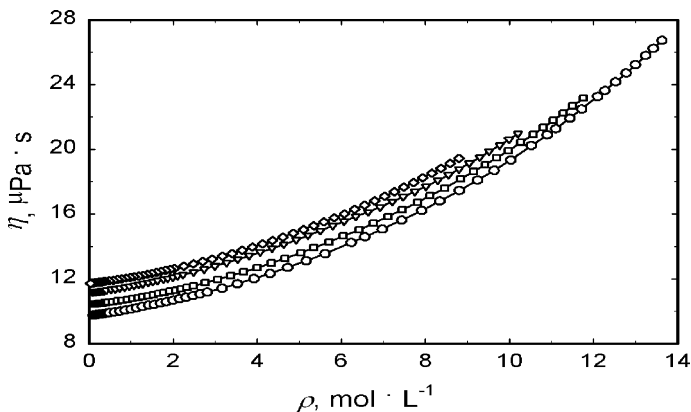
Fig. 8. Viscosity of natural gas sample L as a function of density for several isotherms. (○) 260 K, (□) 280 K, (▽) 300 K, (◇) 320 K.

deviations up to +2 and +1.5% of the measured points of series B from the main series A as well as from the points of the check series C for the 260 and 280 K isotherms could possibly be due to a delayed desorption of the condensate. A condensate deposit on the vibrating wire has to be assumed for the 260 K isotherm because the vibrating-wire viscometer did not work properly. In the case of the isotherms for sample H at 300 K for which the main series A was also performed with decreasing pressure, retrograde condensation cannot occur and good agreement with the results of the check series C was established (Fig. 3). With respect to the performance of the series A and C of the measurements on sample L, a strong effect of the retrograde condensation on the results could not be expected and was not found.

The deviations of the so-called flushing points of series D from the main series A for sample L shown in Figs. 4–6 do not exceed ±0.1%. Thus, effects of adsorption and desorption should be negligible within the experimental errors if their equilibrium can be considered to be adjusted. This should be guaranteed by the measuring procedure chosen.

The density dependence of the viscosity of the natural gas sample L is presented for the four measured isotherms in Fig. 8. The curves correspond to the power series in density of Eq. (2).

5. CONCLUSION

The viscosity of two natural gas samples was determined using a vibrating-wire viscometer at temperatures between 260 and 320 K up to

pressures of 20 MPa. The reproducibility amounts to ±0.2%, whereas the uncertainty is estimated to be ±0.5%, mainly due to the uncertainty in density for the natural gas sample. The decrease in reproducibility, particularly at low temperatures, in comparison with that for measurements on pure gases is due to the retrograde behavior. An essential improvement was achieved if the series of measurements were performed from point to point with increasing pressure. Furthermore, it could be shown that the effects of adsorption and desorption are reasonably small using the same filling procedure.

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